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<b>(21) International Application Number:</b> PCT/US89/05627 <b>(22) International Filing Date:</b> 15 December 1989 (15.12.89)  <b>(30) Priority data:</b> 289,973 22 December 1988 (22.12.88) US  <b>(71) Applicant:</b> GREAT LAKES CHEMICAL CORPORATION [US/US]; P.O. Box 2200, Highway 52 N.W., West Lafayette, IN 47906 (US).  <b>(72) Inventors:</b> FAVSTRITSKY, Nicolai, A. ; 444 Southern Drive, Lafayette, IN 47905 (US). TERMINE, Enrico, J. ; 4444 Antler Way, Lafayette, IN 47905 (US).  <b>(74) Agents:</b> VITTUM, Daniel, W., Jr. et al.; Kirkland & Ellis, 200 East Randolph Drive, Chicago, IL 60601 (US).		<b>(81) Designated States:</b> DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR.  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>
<b>(54) Title:</b> THERMALLY STABLE AND LIGHT STABLE FLAME RETARDANT THERMOPLASTIC POLYOLEFIN AND POLYSTYRENE COMPOSITIONS  <b>(57) Abstract</b>  Thermally stable and light stable flame retardant polyolefin and polystyrene compositions comprise bicyclic phosphate compound(s), halogen-containing flame retardant(s) and polyolefin or polystyrene resins. These compositions exhibit a reduced tendency to develop color, to change melt viscosity or to lose mechanical strength under conditions present during polymer processing and end use.		

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THEMALLY STABLE AND LIGHT STABLE FLAME RETARDANT THERMOPLASTIC  
POLYOLEFIN AND POLYSTYRENE COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention. This invention relates to  
5 thermal and light stable flame retardant thermoplastic  
polyolefin and polystyrene compositions. More  
particularly, this invention relates to thermoplastic  
compositions which are flame retardant and which resist  
thermal degradation or photochemically-induced  
10 degradation. These compositions comprise bicyclic  
phosphate compound(s); halogen-containing flame  
retardant(s); and polystyrene or polyolefin resin.

The compositions produced in accordance with this  
invention have a reduced tendency to develop color, to  
15 change melt viscosity, or to lose mechanical strength  
under conditions that are present during polymer  
processing or end-use.

Description of the Prior Art.

It is known in the art that polystyrene and  
20 polyolefins, such as homopolymers and copolymers of  
polypropylene, polyethylene, and polybutylene, may be  
flame retarded with halogen-containing flame retardants.

Although efficient in suppressing the rate of  
combustion in a resin system, most flame retardants tend  
25 to affect adversely one or more key properties of the  
resin. For example, many flame retardant additives are  
susceptible to thermal and photochemically-induced

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degradation during processing of the thermoplastic resin, or during polymer use conditions.

Evidence of degradation may be seen in several ways. For example, the thermoplastic composition may develop a darkened appearance during processing, indicating polymer or flame retardant chemical decomposition; or the thermoplastic composition may suffer an increase or decrease in melt viscosity, limiting, for example, the recycle of industrial scrap ("regrind") or environmental plastic waste; or the thermoplastic composition may lose mechanical strength, thus reducing the overall service life of the polymeric material.

Many prior art references describe the use of stabilizers, such as antioxidants, hindered phenols, hindered amines, phosphites, and the like, in polystyrene and polyolefins. A general treatise covering this broad topic includes Polymer Stabilization and Degradation, ACS Symposium Series, No. 280, P.P. Klemchuk, ed., American Chemical Society, Washington, D.C. (1985).

However, the selection of a suitable stabilizer for polystyrene and polyolefin resins is not predictable. Stabilizer selection is particularly difficult when flame retardants are employed, exacerbated by the complex interaction between the polymer and the halogen-containing compound.

British Patent No. 889,338 describes the production of bicyclic phosphites, phosphonates, thiophosphates, and selenophosphates. These compositions are said to be

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stabilizers for vinyl halide resins. They are alleged to be useful as heat stabilizers for vinyl chloride resin, and as antioxidants for fats and oils. The British '338 Patent does not show any examples of bicyclic phosphates, nor does it specify the use of bicyclic phosphates, such as pentaerythritol-based bicyclic phosphates of the present invention, which can be employed as a stabilizer for polystyrene or polyolefin resin. Furthermore, the British '338 Patent does not disclose that cyclic phosphates of the present invention could be used with halogen-containing flame retardants to produce flame retardant thermoplastic compositions which resist thermal or photochemically-induced degradation.

British Patent No. 999,793 describes a process to produce organic phosphates by subjecting organic phosphites to reaction with peracetic acid. This patent shows a method for producing the most preferred bicyclic phosphate of the present invention, 2,6,7-trioxa-1-phosphobicyclo[2.2.2]-octane-4-methanol-1-oxide (vide infra), and teaches the use of acetal ring-containing phosphates as plasticizers or functional fluids. The British '793 Patent, however, does not disclose the compositions of the present invention. It does not mention bicyclic phosphates as being useful for flame retardant thermoplastic resins, nor that the most preferred bicyclic phosphate of the present invention can be used with halogen-containing flame retardant additives to yield improved thermoplastic compositions.

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U.S. Patent No. 3,873,496 describes a flame retardant polyester composition which contains 5 to 25 percent of a hydroxymethyl bicyclic phosphate compound as a flame retardant additive. The patentee did not observe the ability of bicyclic phosphates to act as heat or melt stabilizers for thermoplastic resin compositions which employ halogenated compounds as the primary flame retardant additive.

U.S. Patent No. 4,341,694 discloses a composition comprising 2,6,7-trioxa-1-phosphobicyclo[2.2.2]octane-4-methanol-1-oxide and a nitrogen-containing co-additive, which are intumescent and are adaptable to flame retard polyolefins, polyvinylaromatic resins, polycarbonates, PVC and blends thereof. The patentee did not observe any stabilization of the present invention.

Accordingly, a primary object of this invention is to provide thermal and light stable flame retardant thermoplastic polyolefin and polystyrene compositions.

A related object is to provide compositions of the character described which resist thermal degradation or photochemically induced degradation.

A further object is to provide polystyrene or polyolefin resin compositions incorporating bicyclic phosphate compounds and halogenated flame retardants.

25

#### SUMMARY OF THE INVENTION

The foregoing and other objects, advantages and features of the present invention may be achievable with thermal and light stable thermoplastic polyolefin or

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have a reduced tendency to develop color, to change melt viscosity, or to lose mechanical strength under conditions present during polymer processing or in use.

Preferred bicyclic phosphates in accordance with this invention are compounds of Formula (I) where X is OH or OC(O)R'. The most preferred bicyclic compounds are 2,6,7-trioxa-phosphobicyclo[2.2.2]-octane-4-methanol-1-oxide (Compound BCP, that is, Formula [I] when R is H and X is OH), and 2,6,7-trioxa-1-phosphobicyclo[2.2.2]-octane-4-methanol, acetate, 1-oxide (Compound BCP-A, that is, when R is H and X is OC(O)CH<sub>3</sub>).

The halogen-containing flame retardant compound may be any brominated or chlorinated aliphatic or aromatic organic compound that can be used in thermoplastic compositions. Preferred halogen-containing compounds are hexabromocyclododecane, tetrabromobisphenol A, tetrabromobisphenol A bis-(dibromopropylether), dibromo(dibromoethyl)cyclohexane, tetrabromocyclooctane, bis-(dibromonorbornane dicarboximido)ethane, bis-(tetrabromophthalimido)ethane, Diels-Alder adduct of chlorinated cyclopentadiene and unsaturated cycloaliphatic compound, bis-(tribromophenoxyethyl)tetrabromobisphenol A ether, pentabromodiphenyl ether, octabromodiphenyl ether, decabromodiphenyl ether, bis-(tribromophenoxy)ethane, bis-(pentabromophenoxy)ethane, chloropentabromocyclohexane, (tribromophenoxy)-(dibromononylphenoxy)ethane, pentabromoethylbenzene, pentabromododecylbenzene,

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carbonate oligomers of tetrabromobisphenol A, poly(brominated styrene), and brominated polystyrene, poly(brominated phenylene) ether, and mixtures thereof. These halogenated compounds are added to thermoplastic resins at levels such that the resultant resin composition may be rendered flame retardant.

Resins which may be treated in accordance with the invention include thermoplastics such as polystyrene and copolymers of styrene with butadiene and acrylonitrile ("ABS copolymers") and homopolymers and copolymers of polyolefins such as polypropylene, polyethylene, and polybutylene. Polystyrene and polypropylene are preferred thermoplastics in accordance with this invention.

The polystyrene may be any thermoplastic polystyrene, especially impact modified grades, as described in Modern Plastics Encyclopedia, Vol. 63, No. 10A, 74 (1986), or grades suitable for making foamed products. Preferably, the additives of the invention are used with impact grades classified by notched impact values between 0.6 and 3.0 ft-lb/in, and most preferably between 1.0 and 2.5 ft-lb/in.

The polypropylene may be any thermoplastic polypropylene, especially homopolymer type, as described in Modern Plastics Encyclopedia, Vol. 63, No. 10A, 72 (1986), or grades suitable for making foamed products. Preferably, the additives of this invention are used with grades classified by melt flows between 2 and 30 g/10



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min., and most preferably between 4 and 10 g/10 min.

The compositions of this invention also desirably incorporate one or more enhancing agents. Enhancing agents useful in accordance with this invention comprise the oxides and halides of groups IV-A and V-A of the periodic table; organic or inorganic compounds of phosphorus, nitrogen, boron or sulfur; and oxides and halides of, for example, zinc, magnesium and titanium, all as disclosed in U.S. Patent No. 4,016,139.

Preferred enhancing agents in accordance with this invention are the oxides of antimony, arsenic and bismuth, with the oxides of antimony being especially preferred. Antimony trioxide is the most preferred enhancing agent used in the compositions of this invention.

The compositions of this invention may additionally incorporate one or more antioxidants, hindered amine light stabilizers, or acid scavengers. Especially preferred antioxidant is 2,2-bis[[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy)methyl]1,3-propanediyl 3,5,-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoate; especially preferred hindered amine light stabilizer is bis(2,2,6,6-tetramethyl-4-piperidinyl)-sebecate; and especially preferred acid scavenger is magnesium aluminum hydroxy carbonate  $Mg_{4.5}Al_2(OH)_{13}CO_3$ .

The scope of the present invention includes the incorporation of other additives in the composition so far as to produce a particular end result. Such additives include, without limitation, blowing agents, heat

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stabilizers, light stabilizers, plasticizers, pigments, preservatives, ultraviolet light stabilizers, fillers, antioxidants, antistatic agents and other materials well known to those skilled in the art, for example, as described in Modern Plastics Encyclopedia, Vol. 63, No. 10A, McGraw-Hill, Inc. (1986).

The bicyclic phosphates of the present invention may be used alone or as mixtures of any such compounds. When mixtures of bicyclic phosphates are employed, substantially any combinations of amounts and proportions of the individual compounds may be used. The use of Compound BCP and Compound BCP-A is especially preferred in accordance with this invention.

The halogen-containing flame retardants of the present invention may be used alone or as mixtures of any such compounds. When mixtures of halogen-containing phosphates are employed, substantially any combinations of amounts and proportions of the individual compounds may be used. The use of hexabromocyclododecane, tetrabromobisphenol A, chloropentabromocyclohexane, tetrabromobisphenol A bis-(dibromopropylether), dibromo(dibromoethyl)cyclohexane, tetrabromocyclooctane, bis-(dibromonorbornane dicarboximido)ethane, and Diels-Alder adduct of hexachlorocyclopentadiene and cyclooctadiene is especially preferred in accordance with this invention.

Desirably, the bicyclic phosphate compound and

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halogen-containing flame retardant are provided as a mixture useful as an additive which may be added to polystyrene or polyolefin resin compositions. The additive mixture utilizes bicyclic phosphate in  
5 halogen-containing flame retardant in a weight ratio lying in the range of about 0.001 to 0.200, most preferably, about 0.005 to 0.050.

The additive mixture is incorporated into the polymer composition at a level such that the resulting  
10 resin composition is rendered flame retardant. In general, the additive mixture is provided in the flame retardant at a level of about 0.1 - 20.0 percent by weight of the resin composition, preferably about 0.5 - 20.0 percent by weight.

15 Practice of the present invention is illustrated by the following examples.

#### EXAMPLES

The following examples are given to illustrate the invention and should not be construed as limiting its  
20 scope. All percentages are by weight. The term polystyrene refers to polystyrene available from Huntsman Chemical Corporation as PS 3037; the term polypropylene refers to polypropylene available from Himont Chemical Company as Profax 6301; and the term acrylonitrile-  
25 butadiene-styrene refers to acrylonitrile-butadiene-styrene available from Borg Warner Corporation as Cycolac GSM 1000. All flame retardant compositions received a V-2 or V-0 rating as measured by the UL-94 test.

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TABLE I contains examples which illustrate the effectiveness of bicyclic phosphate compound and halogen-containing flame retardant in polypropylene resin to minimize a change in polymer melt viscosity during processing.

05        The thermoplastic compositions were compounded in a 3/4" single screw extruder (L/D 25:1) at 430 °F. The extrudate was pelletized and re-extruded ten times. The melt viscosity of the final extrudate was measured by a melt flow technique.

10        EXAMPLES 1-2 and COMPARATIVE EXAMPLES 1-2

Examples 1-2 are flame retardant polypropylene compositions containing 4.0% hexabromocyclododecane (Flame Retardant HBCD), available under the trademark CD-75P from Great Lakes Chemical Corporation, and, respectively, 0.1% and 0.2% 2,6,7-trioxa-1-phosphobicyclo[2.2.2]octane-4-methanol-1-oxide (Compound BCP).

Comparative Example 1 shows the inherent melt viscosity of a non-flame retardant polypropylene composition which has been subjected to multiple extrusions. Comparative Example 2 shows that Flame Retardant HBCD has a detrimental effect on polymer melt viscosity, as evidenced by an increase in melt flow from 29.3 g/10 min (Comparative Example 1) to 77.1 g/10 min (Comparative Example 2).

25        Surprisingly, when Compound BCP is added to the composition, the damaging effects of Flame Retardant HBCD on the melt viscosity of polypropylene resin are reduced.

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Example 1 and Example 2 show less change in melt flow than Comparative Example 2.

EXAMPLES 3-4 and COMPARATIVE EXAMPLES 3-4

- Examples 3-4 are flame retardant polypropylene compositions containing 0.1% hindered phenolic antioxidant (Compound AO), which is available from Ciba-Geigy Corporation as Irganox 1010, and 0.1% acid scavenger (Compound AS), which is available from Kyowa Chemical Industry as DHT-4A, respectively.
- Examples 3-4 and Comparative Examples 3-4 in TABLE I illustrate also the utility of Compound BCP to inhibit changes in polymer melt viscosity when other additives are present in the thermoplastic resin. Example 3 shows the effectiveness of Compound BCP in the presence of a hindered phenolic antioxidant, and Example 4 shows the effectiveness of Compound BCP in the presence of an acid scavenger.

TABLE I

EXAMPLE NUMBER	BCP ADDITIVE weight %	FLAME RETARDANT		OTHER ADDITIVE		MELT FLOW
		TYPE	AMOUNT weight %	TYPE	AMOUNT weight %	g/10 min ASTM D-1238
0.1	HBCD	4.0	---	---	66.6	
COMP 1	0.0	--	---	--	---	29.3
COMP 2	0.0	HBCD	4.0	--	---	77.1
2	0.2	HBCD	4.0	---	---	70.7

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TABLE I (CONT.)

5	EXAMPLE NUMBER	BCP ADDITIVE weight %	FLAME RETARDANT		OTHER ADDITIVE		MELT FLOW g/10 min ASTM D-1238
			TYPE	AMOUNT weight %	TYPE	AMOUNT weight %	
10	3	0.1	HBCD	4.0	AO	0.1	13.3
	COMP 3	0.0	HBCD	4.0	AO	0.1	75.2
	4	0.1	HBCD	4.0	AS	---	38.2
15	COMP 4	0.0	HBCD	4.0	AS	0.1	40.6

Note: Polypropylene resin, 430°F.

TABLE II contains examples which illustrate the effectiveness of the preferred bicyclic phosphate compound and HBCD in polystyrene resin to minimize a change in polymer melt viscosity during processing.

EXAMPLE 5 and COMPARATIVE EXAMPLES 5-6

Example 5 is a flame retardant polystyrene formulation in accordance with this invention containing 0.1% Compound BCP and 2.0% Flame Retardant HBCD.

Example 5 illustrates an improvement in melt flow over Comparative Example 5 and Comparative Example 6. Thus, Compound BCP is effective in polystyrene when no additional additives are present (Comparative Example 5) or when an acid scavenger is present (Comparative Example 6).

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TABLE II

5	EXAMPLE NUMBER	BCP ADDITIVE weight %	FLAME RETARDANT		OTHER ADDITIVE		MELT FLOW g/10 min ASTM D-1238
			TYPE	AMOUNT weight %	TYPE	AMOUNT weight %	
	5	0.1	HBCD	2.0	--	---	15.8
10	COMP 5	0.0	HBCD	2.0	--	---	>80
	COMP 6	0.0	HBCD	2.0	AS	0.1	22.1

Note: Polystyrene resin, 500°F.

15        TABLE III shows compositions of the present invention which have less tendency to degrade thermally in various polymer systems.

Thermal degradation was measured by formulating compositions in a Brabender Plasticorder mixer (Model  
20 PL-V300) for 21 minutes, 50-70 rpm, and at the temperatures as specified in TABLE III, Footnote 1. The polymer melt was sampled at three minute intervals, and visual inspections of the appearance of the polymer composition were made.

The color and description of the formulated  
25 compositions are listed in Table III, and reflect the appearance of the composition when either the material showed total degradation (that is, developed a black or dark red color or showed signs of decomposition, such as off-gassing), or when the 21 minute interval of the test was attained.

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EXAMPLES 6-10 and COMPARATIVE EXAMPLES 7-12

Examples 6-9 are flame retardant polystyrene compositions containing 0.2% Compound BCP and 4.0%, respectively, Flame Retardant HBCD; dibromo(dibromoethyl) cyclohexane (Flame Retardant TBCH), available from Ethyl Corporation as BCL-462; Diels-Alder adduct of hexachlorocyclopentadiene and cyclooctadiene (Flame Retardant CBCO), available from Occidental Corporation as Dechlorane Plus; and monochloropentabromocyclohexane (Flame Retardant CBCH), available from Dow Chemical Corporation as FR-651.

Example 10 is a flame retardant polystyrene composition containing 0.8% Compound BCP and 16.0% tetrabromobisphenol A (Flame Retardant TBBP), available from Great Lakes Chemical Corporation as BA-59P.

Examples 6-10, as supported by comparisons to Comparative Examples 8-12 (specified in Table III) illustrate polystyrene compositions which resist thermal degradation and have less tendency to develop color under processing conditions. Comparative Example 7 shows the inherent color development of non-flame retardant polystyrene resin which has been subjected to the test procedures.

Examples 6-10 illustrate also that Compound BCP is effective in the presence of various halogen-containing flame retardant additives.

EXAMPLE 11

Example 11 is a flame retardant polystyrene compo-



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sition containing 0.2% acetate derivative of Compound BCP (designated Compound BCP-A) and 4.0% Flame Retardant HBCD. Example 11 is an illustration of a bicyclic phosphate other than Compound BCP which is within the scope of this invention.

5           EXAMPLE 12 and COMPARATIVE EXAMPLES 13-14

Example 12 is a flame retardant acrylonitrile-butadiene-styrene ("ABS") composition containing 0.5% Compound BCP, 4.0%  $\text{Sb}_2\text{O}_3$ , and 16.0% Flame Retardant TBBP.

Example 12, as supported by comparison to Comparative  
10 Examples 14 (specified in Table III), is an illustration of utility of the present invention in ABS resin. Comparative Example 13 shows the inherent color development of non-flame retardant ABS resin which has been subjected to the test procedures.

15           EXAMPLES 13-14 and COMPARATIVE EXAMPLES 15-17

Examples 13-14 are flame retardant polypropylene compositions containing 0.5% Compound BCP, 1.0%  $\text{Sb}_2\text{O}_3$ , and, respectively, 3.0% tetrabromobisphenol A bis(dibromopropylether) (Flame Retardant TBPE) and 5.0% Flame  
20 Retardant HBCD.

Examples 13-14, as supported by comparison to Comparative Examples 16-17 (specified in Table III), illustrate the effectiveness of the present invention to reduce the tendency for discoloration in flame retardant  
25 polypropylene compositions. Comparative Example 15 shows the inherent color development of non-flame retardant polypropylene resin which has been subjected to the test procedures.

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TABLE III

5	EXAMPLE NUMBER	BCP ADDITIVE weight %	FLAME RETARDANT		AMOUNT weight %	COLOR <sup>2</sup>	DESCRIPTION
			RESIN TYPE <sup>1</sup>	TYPE			
10	6	0.2	A	HBCD	4.0	0	TRANSPARENT
	COMP 7	0.0	A	--	---	0	TRANSPARENT
	COMP 8	0.0	A	HBCD	4.0	10	OPAQUE
15	7	0.2	A	TBCH	4.0	2	TRANSPARENT
	COMP 9	0.0	A	TBCH	4.0	10	OPAQUE
	8	0.2	A	CBCO	4.0	0	OPAQUE
	COMP 10	0.0	A	CBCO	4.0	3	OPAQUE
	9	0.2	A	CBCH	4.0	4	OPAQUE
	COMP 11	0.0	A	CBCH	4.0	10	OPAQUE
20	10	0.8	A	TBBP	16.0	2	OPAQUE
	COMP 12	0.0	A	TBBP	16.0	8	OPAQUE
	11	0.2	A	HBCD	4.0	2	TRANSPARENT
25	12	0.5	B	TBBP	16.0	5	OPAQUE
	COMP 13	0.0	B	--	---	1	OPAQUE
	COMP 14	0.0	B	TBBP	16.0	8	OPAQUE
30	13	0.5	C	TBPE	3.0	6	OPAQUE
	COMP 15	0.0	C	--	---	1	OPAQUE
	COMP 16	0.0	C	TBPE	3.0	10	OPAQUE
	14	0.5	C	HBCD	5.0	1	OPAQUE
	COMP 17	0.0	C	HBCD	5.0	10	OPAQUE

NOTE 1: A) Polystyrene resin, 450°F; B) Acrylonitrilebutadiene-styrene resin, 4.0% Sb<sub>2</sub>O<sub>3</sub>, 500°F; C) Polypropylene, 1.0% Sb<sub>2</sub>O<sub>3</sub>, 430°F.

NOTE 2: 0=colorless; 1=white; 2=light yellow; 3=yellow; 4=dark yellow; 5=light tan; 6=tan; 7=dark tan; 8=brown; 9=dark brown; 10=black, red or decomposed.

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TABLE IV shows polypropylene compositions of the present invention which have less tendency to lose mechanical strength, when such compositions are exposed to radiation.

5 Thermoplastic compositions were compounded and injection molded into test specimens, measuring 5.0" x 0.5" x 0.062". The ends of the test specimens were clamped together, placed in an Xenon Arc Weatherometer (Atlas Model Ci-35), and irradiated according to ASTM  
10 D-4459 procedures for 3000 hours. The test specimens were observed periodically for signs of cracks or crazing. The time at which failure occurred was noted.

EXAMPLES 15-16 and COMPARATIVE EXAMPLES 18-19

15 Examples 15-16 are flame retardant polypropylene compositions containing 0.5% Compound BCP, 10.0% Flame Retardant TBPE, 3.3%  $\text{Sb}_2\text{O}_3$ , and, respectively, 0.5% hindered amine light stabilizer (Compound HALS), available from Ciba-Geigy Corporation as TINUVIN 770, and 0.5%  
20 Compound AS.

Examples 15-16, as supported by comparison to Comparative Examples 18-19 (specified in Table IV), illustrate the effectiveness of the present invention to reduce the tendency for photochemically-induced  
25 mechanical failure in flame retardant polypropylene compositions.

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TABLE IV

EXAMPLE NUMBER	BCP ADDITIVE weight %	FLAME RETARDANT		OTHER ADDITIVE		TIME TO STRESS FAILURE hours
		TYPE	AMOUNT weight %	TYPE	AMOUNT weight %	
15	0.5	TBPE	10.0	HALS	0.5	2900
10 COMP 18	0.0	TBPE	10.0	HALS	0.5	2500
16	0.5	TBPE	10.0	AS	0.5	>3000
COMP 19	0.0	TBPE	10.0	AS	0.5	150
Polypropylene resin and 3.3% $\text{Sb}_2\text{O}_3$ .						

TABLE V shows polypropylene compositions of the present invention which have less tendency to discolor, when such compositions are exposed to radiation.

Thermoplastics compositions were compounded, injection molded into 3.0" x 1.0" x 0.125" test specimens, and irradiated in a Xenon Arc Weatherometer (Atlas Model Ci-35), according to ASTM D-4459 procedures for 2000 hours. Changes in color were measured as Delta E values, according to ASTM-2244 procedures.

#### EXAMPLES 17-20 and COMPARATIVE EXAMPLES 20-22

Examples 17-18 are flame retardant polypropylene compositions containing 3.3%  $\text{Sb}_2\text{O}_3$ , 10.0% Flame Retardant TBPE, and, respectively, 1.0% BCP Compound and 0.5% Compound BCP.

Examples 19-20 are flame retardant polypropylene compositions containing 0.5% Compound BCP, 10.0% Flame

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Retardant TBPE, and, respectively, 0.5% hindered amine light stabilizer Compound HALS and 0.5% alkytin-containing stabilizer (Compound TLS), available from Witco Chemical Company as Mark 1413.

5        Examples 17-20, as supported by comparison to Comparative Examples 20-22 (specified in Table V), illustrate the effectiveness of the present invention to reduce the tendency for photochemically-induced discoloration in flame retardant polypropylene composi-  
10    tions.

TABLE V

15	EXAMPLE NUMBER	BCP ADDITIVE weight %	FLAME RETARDANT		OTHER ADDITIVE		COLOR LIGHT STABILITY Delta E
			TYPE	AMOUNT weight %	TYPE	AMOUNT weight %	
	17	1.0	TBPE	10.0	---	---	4.90
20	18	0.5	TBPE	10.0	---	---	4.08
	COMP 20	0.0	TBPE	10.0	---	---	7.90
	19	0.5	TBPE	10.0	HALS	0.5	2.03
	COMP 21	0.0	TBPE	10.0	HALS	0.5	4.05
	20	0.5	TBPE	10.0	TLS	0.5	3.02
25	COMP 22	0.0	TBPE	10.0	TLS	0.5	3.27

Polypropylene resin and 3.3% Sb<sub>2</sub>O<sub>3</sub>.

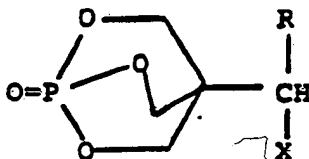
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CLAIMS

1. A thermally stable and light stable thermoplastic resin composition comprising a polyolefin or polystyrene resin and a mixture comprising;

- 5                   at least one halogen-containing flame retardant;  
and  
                  at least one bicyclic phosphate compound of the  
formula:

10



where X is OH, OR', or OC(O)R'; R is H or a saturated or  
15   unsaturated straight-chain or branched-chain C<sub>1</sub>-C<sub>17</sub> alkyl;  
and R' is a saturated or unsaturated straight-chain or  
branched chain C<sub>1</sub>-C<sub>17</sub> alkyl.

2. A composition, as claimed in claim 1, wherein  
the halogen-containing flame retardant is a member  
20   selected from the group consisting of hexabromocyclododecane, tetrabromobisphenol A, chloropentabromocyclohexane, tetrabromobisphenol A bis-(dibromopropylether), dibromo(dibromoethyl)cyclohexane, tetrabromocyclooctane, bis-(dibromonorbornane dicarboximido)ethane, Diels-Alder  
25   adducts of hexachlorocyclopentadiene and cyclooctadiene  
and mixtures thereof.

3. A composition, as claimed in claim 1, wherein  
the bicyclic phosphate compound is 2,6,7-trioxa-phospho-

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bicyclo[2.2.2]-octane-4-methanol-1-oxide; or 2,6,7-trioxa-1-phosphobicyclo[2.2.2]-octane-4-methanol, acetate, 1-oxide.

4. A composition, as claimed in claim 1, wherein  
5 the resin is a member selected from the group consisting of polystyrene, acrylonitrile-butadiene-styrene resin, and polyethylene, polypropylene and polybutylene homo- and copolymers.

5. A composition, as claimed in claim 4, wherein  
10 the member is polypropylene or polystyrene.

6. A composition, as claimed in claim 1, wherein the weight ratio of bicyclic phosphate compound to halogen-containing flame retardant lies in the range of about 0.001 to 0.200.

15 7. A composition, as claimed in claim 1, wherein the mixture of bicyclic phosphate compound and halogen-containing flame retardant is provided in the resin composition at a level lying in the range of about 0.1 - 20.0 percent by weight of the overall composition.

20 8. A composition, as claimed in claim 1, and further comprising at least one member selected from the group consisting of antioxidants, hindered amine light stabilizers, and acid scavengers.

9. A composition, as claimed in claim 8, wherein  
25 the antioxidant is 2,2-bis[[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]1,3-propanediyl 3,5,-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoate.

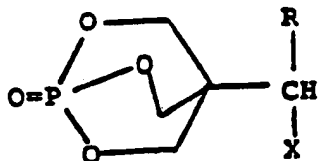
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10. A composition, as claimed in claim 8, wherein the hindered amine light stabilizer is bis-(2,2,6,6-tetramethyl-4-piperidinyl)-sebecate.

11. A composition, as claimed in claim 8, wherein the acid scavenger is magnesium aluminum hydroxy carbonate  $Mg_{4.5}Al_2(OH)_{13}CO_3$ .

12. A flame retardant stabilizing additive mixture for polyolefin or polystyrene resin compositions comprising:

- a halogen-containing flame retardant; and  
a bicyclic phosphate compound of the formula:



where X is OH, OR', or OC(O)R'; R is H or a saturated or unsaturated straight-chain or branched-chain  $C_1-C_{17}$  alkyl; and R' is a saturated or unsaturated straight-chain or branched chain  $C_1-C_{17}$  alkyl.

13. A mixture, as claimed in claim 12, wherein the flame retardant is a member selected from the group consisting of hexabromocyclododecane, tetrabromobisphenol A, chloropentabromocyclohexane, tetrabromobisphenol A bis-(dibromopropylether), dibromo(dibromoethyl)cyclohexane, tetrabromocyclooctane, bis-(dibromonorbornane dicarboximido)ethane, Diels-Alder adducts of hexachlorocyclopentadiene and cyclooctadiene and mixtures thereof.



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14. A mixture, as claimed in claim 12, wherein the bicyclic phosphate compound is 2,6,7-trioxa-phosphobicyclo [2.2.2]-octane-4-methanol-1-oxide; or 2,6,7-trioxa-1-phosphobicyclo[2.2.2]-octane-4-methanol, acetate, 1-oxide.

5 15. A mixture, as claimed in claim 12, wherein the weight ratio of bicyclic phosphate compound to halogen-containing flame retardant lies in the range of about 0.001 to 0.200.

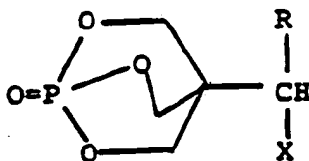
## AMENDED CLAIMS

[received by the International Bureau  
on 25 May 1990 (25.05.90);  
original claim 4 cancelled; original claims  
1,5 and 12 amended; other claims unchanged (4 pages)]

1. (Amended) A thermally stable and light stable  
thermo-plastic resin composition comprising a resin selected  
from the group consisting of polystyrene, acrylonitrile-  
butadiene-styrene resin, and polyethylene, polypropylene and  
polybutylene homo- and copolymers and a mixture comprising:

at least one halogen-containing flame  
retardant; and

at least one bicyclic phosphate compound of the  
formula:



where X is OH, OR', or OC(O)R'; R is H or a saturated or  
unsaturated straight-chain or branched-chain C<sub>1</sub>-C<sub>17</sub> alkyl; and  
R' is a saturated or unsaturated straight-chain or branched  
chain C<sub>1</sub>-C<sub>17</sub> alkyl.

2. A composition, as claimed in claim 1, wherein  
the halogen-containing flame retardant is a member selected  
from the group consisting of hexabromocyclododecane,  
tetrabromobisphenol A, chloropentabromocyclohexane,  
tetrabromobisphenol A bis-(dibromopropylether),  
dibromo(dibromoethyl)cyclohexane, tetrabromocyclooctane,  
bis-(dibromonorbornane dicarboximido)ethane, Diels-Alder  
adducts of hexachlorocyclopentadiene and cyclooctadiene and  
mixtures thereof.

3. A composition, as claimed in claim 1, wherein the bicyclic phosphate compound is 2,6,7-trioxa-phospho-bicyclo[2.2.2]-octane-4-methanol-1-oxide; or 2,6,7-trioxa-1--phosphobicyclo[2.2.2]-octane-4-methanol, acetate, 1-oxide.

5 4. (Cancelled.)

5. (Amended) A composition, as claimed in claim 1, wherein the resin is polypropylene or polystyrene.

6. A composition, as claimed in claim 1, wherein the weight ratio of bicyclic phosphate compound to  
10 halogen-containing flame retardant lies in the range of about 0.001 to 0.200.

7. A composition, as claimed in claim 1, wherein the mixture of bicyclic phosphate compound and halogen-containing flame retardant is provided in the resin  
15 composition at a level lying in the range of about 0.1 - 20.0 percent by weight of the overall composition.

8. A composition, as claimed in claim 1, and further comprising at least one member selected from the group consisting of antioxidants, hindered amine light stabilizers,  
20 and acid scavengers.

9. A composition, as claimed in claim 8, wherein the antioxidant is 2,2-bis[[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopro-  
25 poxy]methyl]1,3-propanediyl 3,5,-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoate.

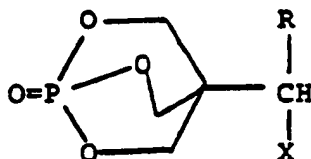
10. A composition, as claimed in claim 8, wherein the hindered amine light stabilizer is bis-(2,2,6,6-tetramethyl-4-piperidiny1)-sebacate.

11. A composition, as claimed in claim 8, wherein the acid scavenger is magnesium aluminum hydroxy carbonate  $Mg_{4.5}Al_2(OH)_{13}CO_3$ .

12. (Amended) A flame retardant stabilizing additive mixture for resin compositions selected from the group consisting of polystyrene, acrylonitrile-butadiene-styrene resin, and polyethylene, polypropylene and polybutylene homo- and copolymers comprising:

a halogen-containing flame retardant; and

a bicyclic phosphate compound of the formula:



where X is OH, OR', or OC(O)R'; R is H or a saturated or unsaturated straight-chain or branched-chain  $C_1$ - $C_{17}$  alkyl; and R' is a saturated or unsaturated straight-chain or branched chain  $C_1$ - $C_{17}$  alkyl.

13. A mixture, as claimed in claim 12, wherein the flame retardant is a member selected from the group consisting of hexabromocyclododecane, tetrabromobisphenol A, chloropentabromocyclohexane, tetrabromobisphenol A bis-(dibromopropylether), dibromo(dibromoethyl)cyclohexane,

tetrabromocyclooctane, bis-(dibromonorbornane dicarboximido)-ethane, Diels-Alder adducts of hexachlorocyclopentadiene and cyclooctadiene and mixtures thereof.


14. A mixture, as claimed in claim 12, wherein the  
5 bicyclic phosphate compound is 2,6,7-trioxa-phosphobicyclo  
[2.2.2]-octane-4-methanol-1-oxide; or 2,6,7-trioxa-1-  
phosphobicyclo[2.2.2]-octane-4-methanol, acetate, 1-oxide.

15. A mixture, as claimed in claim 12, wherein the  
weight ratio of bicyclic phosphate compound to  
10 halogen-containing flame retardant lies in the range of about  
0.001 to 0.200.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US89/05627

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC (5) A23J 7/00; C07F 9/02, 9/10; C08K 5/34		
U.S. CL. 252/403; 524/102, 119		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
U.S.	252/403; 524/102, 119	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>*</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US, A, 4,118,352 (HABERLEIN ET AL) 3 OCTOBER 1978 See column 3, line 5 through column 8, line 21.	1-15
Y	US, A, 3,293,327 (HECHENBLEIKNER ET AL) 20 DECEMBER 1966 See column 1, line 20 through column 2, line 61.	1-15
Y	US, A, 3,840,494 (MURAYAMA ET AL) 8 OCTOBER 1974 See column 1, line 24 through column 6, line 29.	1-15
Y	US, A, 4,016,139 (ANDERSON ET AL) 5 APRIL 1977 See column 10, line 34.	1-15
Y	US, A, 4,299,759 (MIYATA ET AL) 10 NOVEMBER 1981	1-15
Y	JP, A, 61-106641 (MARUBISHI YUKA KOGY KK) 24 MAY 1986 See abstract.	1-15
Y	EP, A, 0116200 (MITSUBISHI PETROCHEMICAL CO., LTD) 22 AUGUST 1984 See pages 7, 8, and 16.	1-15
Y	JP, A, 53-71160 (SHOWA DENKO KK) 24 JUNE 1978 See abstract.	1-15
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>*</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
21 MARCH 1990		29 MAR 1990
International Searching Authority		Signature of Authorized Officer
ISA/US		 KRIELLION MORGAN HO NGUYEN